

NANOSTRUCTURED POLYMER MEMBRANES FOR CHEMICAL PROTECTIVE CLOTHING

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ABSTRACT

A series of materials were evaluated for their potential use as breathable (high water transport) barriers (low chemical agent transport) for military and civilian protective clothing apparel. The vapor transmission rates and effective permeabilities of water and dimethyl methyl phosphonate (DMMP, simulant for chemical agent Sarin) through commercial and experimental polymeric membranes were measured using a modified ASTM method E-96-95. A variety of different materials from different companies were examined, unfortunately some can not be named due to proprietary restrictions. Materials examined included expanded PTFE, Nafion 117®, sulfonated polystyrene-polyethylene-random-polybutylene-polystyrene, sulfonated polystyrene-polyisobutylene-polystyrene, as well as four experimental and commercial membranes (A, B, C, and D). Results demonstrate that laminated membrane A had the highest breathability (effective permeability of water vapor), however experimental laminated material C possessed the highest selectivity with sufficient breathability, where selectivity is defined as the ratio of water permeability to DMMP permeability. Based on the results from this study, material C presents the greatest potential for a breathable barrier material for a chemical protective clothing application.

1. INTRODUCTION

Chemical/biological protective clothing technology remains a high priority among people responsible for the safety of US military personnel. Not just from the obvious point of exposure to chemical or biological agents abroad and at home, but also from another, less often considered, but still important safety factor: breathability. Until recently the main goal in the development of chemical/biological protective clothing was to maximize protection. In the past, one of the more commonly used materials for this application was butyl rubber working on principle of total blockage. Butyl rubber is an effective barrier to

most harmful agents at certain thicknesses, but it has certain disadvantages. Wearing garments manufactured from this material in combat or in other situations which involves physical activity is not practical, since the lack of breathability of this material causes heat fatigue and exhaustion [Lee et al, 1996]. A different approach for protection against chemical/biological threats is sorption materials. Protective suits such as MOPP (Military Oriented Protective Posture) suit and JSLIST (Joint Service Lightweight Integrated Suit Technology) work on principle of capturing toxic materials with fillers like activated carbon. JSLIST, is more breathable, but it is not provide as much protection as butyl rubber, still heavy, bulky and working in the suit is limited to about 45min/hr. [Siegrist, 2002]

A completely different approach to the problem of chemical/biological protection is the concept of semi-permeable membranes. That would be materials that allow passage of moisture (perspiration), but block harmful molecules and organisms. Materials like that will offer protection in the hostile environment without causing significant heat fatigue and exhaustion. A number of such semi-permeable membranes are being developed in industry and at ARL.

The scope of this work was to examine a series of semi-permeable membranes in order to evaluate their potential usefulness as a breathable, yet agent resistant material for military and civilian clothing. This study examines the permeation of water vapor and the permeation of dimethylmethylphosphonate (DMMP) vapor through a variety of materials to determine the best candidates that are both breathable and protective. DMMP is chemically similar to the nerve agent Sarin (GB) and is often used to imitate the behavior of chemical agents when the usage of actual agents is cost prohibitive due to safety concerns. Materials examined in this study include some commercial materials as well as a number experimental materials under development both at ARL and other laboratories. Due to proprietary restriction and other legal considerations, it was decided that four materials can not be named and will

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be referred to as materials A, B, C, and D with manufacturers referred to by the same letter.

2. EXPERIMENTAL

2.1 Materials

Materials evaluated in this study are listed in Table 1. Sulfonated poly(styrene-isobutylene-styrene) (S-SIBS) at both 58 and 85 mole percent sulfonation, referred to as S-SIBS-58 and S-SIBS-85 in Table 1, respectively, was sulfonated at ARL and the details of this procedure can be found elsewhere [Elabd and Napadensky, 2004]. Mole percent sulfonation is defined as moles of sulfonic acid per moles of styrene repeat unit and was determined by elemental analysis. The unsulfonated polymer was provided by Kuraray Co., Ltd., Tsukuba research laboratories, with the reported properties: 30.84 wt% styrene, 0.95 specific gravity, $M_w = 71,920$ g/mol, $M_n = 48,850$ g/mol, and polydispersity index (PDI) = 1.47. Sulfonated poly(styrene-ethylene-*ran*-butylene-styrene) (S-SEBS) at both 59 and 93 mole percent sulfonation, referred to as S-SEBS-59 and S-SEBS-93 in Table 1, respectively, was sulfonated at ARL and the general details of this procedure can be found elsewhere [Weiss et al. 1991, Elabd et al, 2003]. Unsulfonated poly(styrene-ethylene-*ran*-butylene-styrene) was provided by Kraton Polymers. S-SEBS-50 is a poly(styrene-ethylene-*ran*-butylene-styrene) sulfonated to 45-55% that was purchased from Sigma-Aldrich as a solution and cast into films at Natick Soldier Command Center. Other materials in this study included an expanded PTFE membrane, Nafion 117® (DuPont), and another four materials A, B, C and D from corresponding companies. In addition, other chemicals used in these experiments were as follows: Water (J. T. Baker, HPLC grade), dimethylmethylphosphonate (Lancaster Synthesis, 97%), Drierite® (Anhydrous Calcium Sulfate, 97%, W.A. Hammond Drierite Co.), toluene (EM Science, 99.5%), and hexanol (J.T. Baker).

2.2 Permeation Equipment

Equipment used for vapor permeation experiments consisted of a temperature controlled oven with a nitrogen gas sweep passing through a Drierite® packed column. Aluminum trays with Drierite® were also placed inside the oven to maintain a low relative humidity (approximately 10%). In addition, an analytical balance (precision= ± 0.0001 g) was used to measure weight loss and a digital micrometer was used to measure the thickness of each membrane (precision= ± 1.2 μm).

2.3 Membrane Preparation

Membranes developed at ARL (S-SIBS-58, S-SIBS-85, S-SEBS-59, S-SEBS- 93) were prepared by solution casting in Teflon® petri dishes at 2.5% w/v of polymer in 85/15 w/w toluene/hexanol. All membranes were cast in open air for 2 weeks, then annealed in a vacuum oven at 50° C for one or two weeks to remove residual solvent. All other membranes were used as received.

Table 1. List of evaluated materials and their thickness.

Material Name	Source / Manufacturer	Sample Thickness (μm)
S-SIBS-58	ARL	103 - 159
S-SIBS-85	ARL	89 - 115
S-SEBS-59	ARL	129 - 188
S-SEBS-93	ARL	111 - 174
S-SEBS-50	Aldrich	119 - 204
A (cloth laminate)	A	264 - 372
Expanded PTFE	Natick SCC	43 - 48
B	B	13 - 16
C	C	179 - 187
D	D	39 - 42
Nafion 117®	DuPont	181 - 186

2.4 Vapor Permeation Procedure

2.4.1. Cap Loading

20 ml vials, with open-top caps (VWR) and Teflon® lined septa with a 14 mm hole cut in the center of the septa to match the hole in the cap, were used (Figure 1). Membranes were cut into circles with a 22 mm diameter, the size of the original septa. The thickness of each individual membrane was measured with a digital micrometer. Membranes were placed inside the cap with the cored septa placed behind to provide air tight seal.

For samples, A and C, the polymeric membranes which are laminated onto cloth were loaded into the cap assembly with the cloth side positioned toward the permeant for DMMP vapor permeation and positioned away from the permeant for water vapor permeation.

2.4.2 Vapor Permeation

Vapor permeation experiments were conducted based on the ASTM E 96-95 (Standard Test Methods for Vapor Transmission of Materials) procedure. An oven, with nitrogen gas purge passed through a desiccant trap, was stabilized at 35°C and 10% relative humidity (RH). Vials were filled with 10-15 ml of liquid (water or DMMP) and placed in oven to equilibrate for about 24 hr. Vials were removed; regular caps were replaced with membrane lined caps shown in Figure 1. The total assembly weight was recorded and the vials were placed back into the oven to initiate the experiments. The complete membrane/vial assembly is shown in Figure 1.

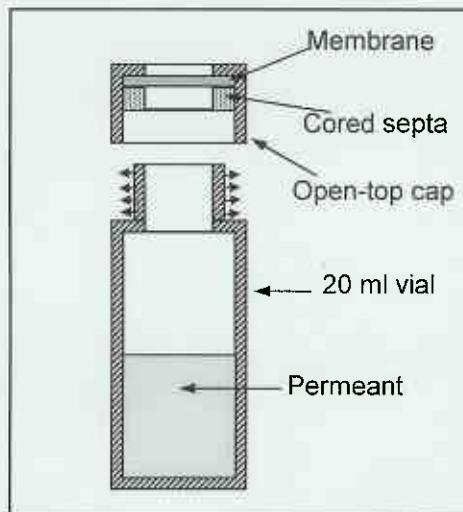


Figure 1. Complete vial assembly used for vapor permeation experiments.

Vial weight, temperature, and humidity inside the oven were recorded every 24 hr until a sufficient amount of data was collected to determine constant rate of weight loss for each vial (steady-state). Relative humidity (RH) remained constant at 10% throughout the duration of the experiment. When using water as a permeant, the conditions were 100% RH on one side of the membrane (inside the vial) and 10% RH on the other side (outside the vial). The concentration gradient provided the driving force for vapor transport. Experiments with DMMP vapor were at 100% DMMP saturation (6.77 mm Hg) on one side of the membrane (inside the vial) and 0% DMMP on the other side or outside the vial.

Three experiments were conducted for each membrane and the values calculated for each membrane are the average and standard deviation of those experiments.

3. Results and Discussion

3.1 Theory

Vapor transfer rate (VTR) is defined as steady state vapor transport rate per unit area and can be expressed as follows:

$$VTR = \frac{G}{(t * A)} \quad (1)$$

where G is weight of penetrant, t is time, and A is cross-sectional area. For this experiment, the cross-sectional area is 0.000154 m^2 , since the diameter is constant at 14mm. G/t can be regressed from the steady state portion of the weight loss data versus time, as shown in Figure 2.

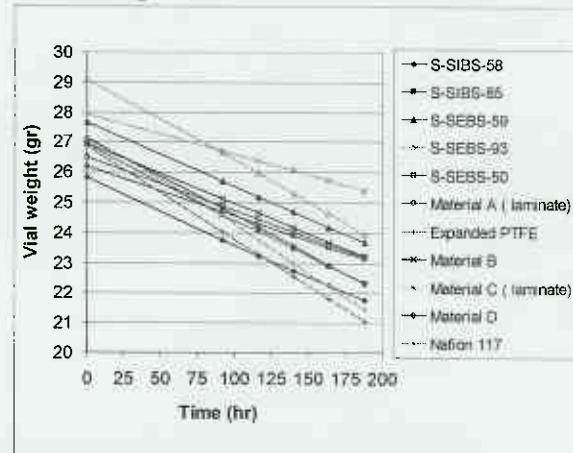


Figure 2. Weight loss during water vapor permeation experiments.

After calculating G/t from the data, VTR can be obtained using Equation 1.

VTR provides transport rate for a given penetrant through a membrane. However, VTR does not account for the thickness of the membrane effectively. More specifically, VTR will have different values for the same material at different thicknesses. To accurately compare materials independent of the processing thickness, an effective permeability must be calculated. Effective permeability (P_{eff}) can be expressed as:

$$P_{\text{eff}} = \frac{L * \text{VTR}}{S * (P_1 - P_2)} \quad (2)$$

where S is the saturation vapor pressure at the test temperature (mmHg), P_1 is the partial pressure or relative humidity on the challenge side, P_2 is partial pressure on the exit side, and L is the sample thickness (m). For laminated samples (materials A and C), L was taken to be thickness of the full system, cloth and all the layers of lamination. Saturation vapor pressure for water at 35° C is 41.175 mm Hg [6] and for DMMP at 35° C is 6.77 mm Hg. The DMMP vapor pressure was determined by interpolating from known values at 25° C and 65° C [Merck Index, 2001].

3.2 VTR and P_{eff}

Figures 3 and 4 show water VTR and P_{eff} results for all of the materials studied. Since breathability is one of the key goals, it is tempting to concentrate on materials with a high water VTR. However, since VTR values do not account for sample thickness, a high VTR value does not necessarily signify sufficient breathability. Good examples include expanded PTFE, material B, and material D. All three samples have high VTRs (Figure 3), but when their thicknesses are taken into consideration, their effective permeability, P_{eff} (breathability) is significantly lower than other materials (Figure 5)

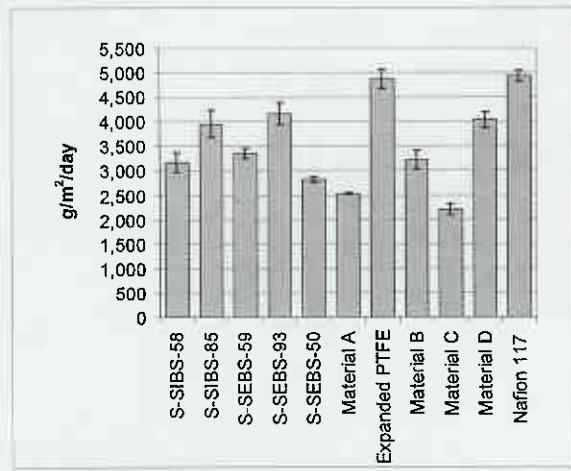


Figure 3. Water vapor transmission rate.

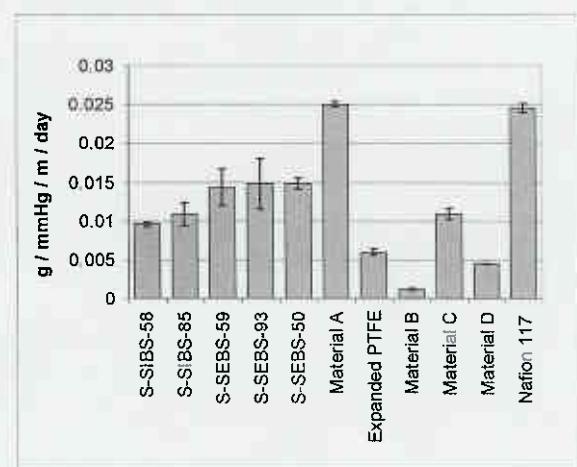


Figure 4. Water effective permeability results.

Figures 5 and 6 show VTR and P_{eff} results for DMMP, respectively. DMMP simulates the nerve agent Sarin and the optimum material is one that minimizes DMMP transfer for good barrier properties against chemical agents. Figure 6 shows that materials B, C and D have the lowest values of DMMP P_{eff} and would provide the best protection against chemical agents.

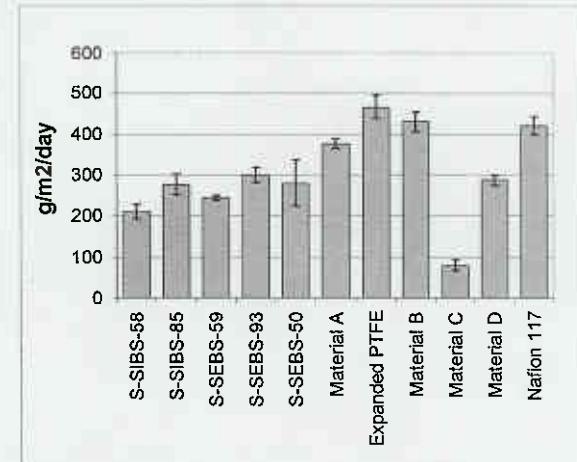


Figure 5. DMMP vapor transmission rate

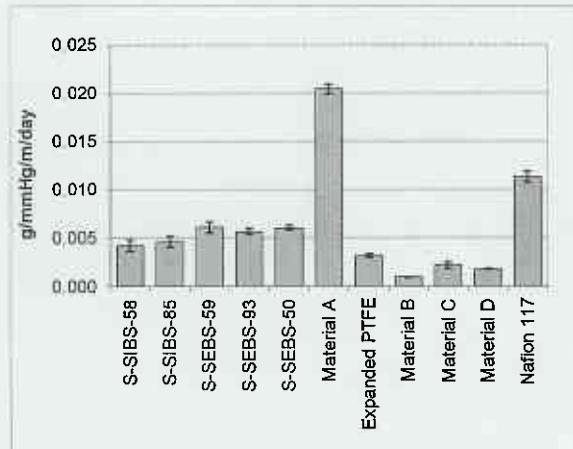


Figure 6. DMMP effective permeability results.

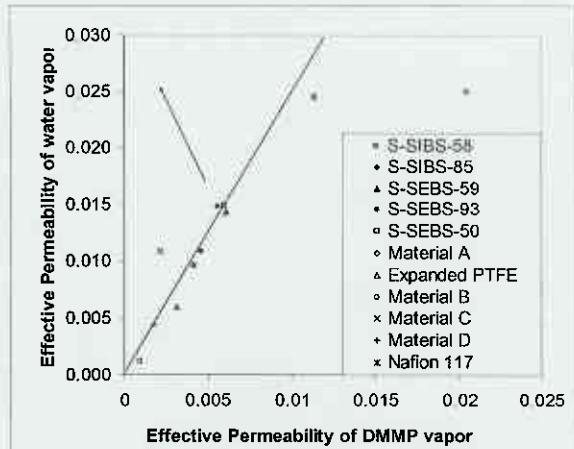


Figure 7. Relative performance of materials based on effective permeability.

3.3 Selectivity

The goal for chemical and biological defense is to identify materials that will provide sufficiently high water transport (breathability) to reduce heat fatigue, and sufficiently low DMMP transport to reduce personnel risk from harmful agents. The performance of these materials can be examined by plotting $P_{\text{eff}}(\text{DMMP})$ vs. $P_{\text{eff}}(\text{WATER})$, as shown in Figure 7.

An actual numerical value of ratio of effective permeabilities is defined as selectivity (α):

$$\alpha = \frac{P_{\text{eff}}(\text{WATER})}{P_{\text{eff}}(\text{DMMP})} \quad (3)$$

where a high value would be desired for a breathable protective material. This is the slope of the trend line shown in Figure 8. The upper left corner of this plot is where an ideal material for breathable protective clothing would be located. This corresponds to a very high water transport and simultaneously very low agent transport or a high selectivity.

Selectivity values for materials examined in these experiments are shown in Figure 8.

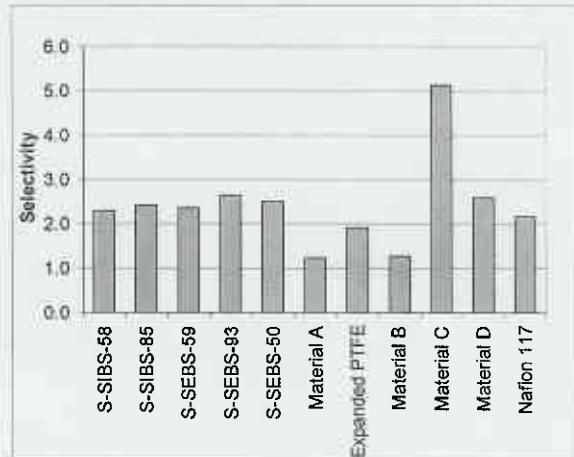


Figure 8. Selectivity of materials.

Selectivity does not account for actual amount of penetrant going through membrane. A material that has high values for effective permeation for both penetrants may have the same selectivity as a material that has low values for both penetrants. Therefore, generally selectivity cannot be used as a final criteria, but rather should be used in conjunction with P_{eff} (water vapor). However, in this study, the water vapor transport for all materials (Figure 3 and 4) provide sufficient breathability, and therefore, materials with the highest selectivities have the desired properties for breathable protective clothing. Figure 8 shows that material C has a selectivity that is more than double compared to the other materials in this study.

4. Conclusion

In this study, the water vapor transmission rate, effective permeability, and selectivity of water vapor and DMMP vapor (simulant for chemical warfare agent) were measured for a variety of commercial and experimental candidate materials for evaluation as a breathable barrier for protective clothing. Material C has sufficient water vapor permeability (breathability) and a selectivity (5.12) that is more than double compared to the rest of the materials evaluated. If high selectivity is used as an indicator, then out of the materials evaluated in this study, this one has a good potential for use as a breathable barrier for protective clothing. Of course, there are still other factors that need to be considered, such as durability, price, weight, processability, and other physical properties. Over all, this preliminary study indicates that further research on the synthesis and testing of new semi-permeable materials may produce more efficient breathable barriers not only protective clothing for the military, but also for apparel for a variety of other applications.

5. References

Lee, B. T., T. W. Yang, and E. Wilusz. "Moisture Effects on Isobutylene-Isoprene Copolymer-Based Composite Barrier. 1. Moisture Diffusion and Detection." *Polymer Engineering & Science*, vol 36, no. 9, p. 1217, 1996.

David Siegrist, "Chemical – Biological Warfare: Protective Measures". Jane's Defence Weekly. April 17, 2002

Elabd, Y.A.; Napadensky, E. "Sulfonation and Characterization of Poly(styrene-isobutylene-styrene) Triblock Copolymers at High Ion-Exchange Capacities", *Polymer*, (submitted for publication, 2003).

Weiss,R.A., Sen,A., Willis,C.L., Pottick,L.A. in "Block copolymer ionomers: 1 Synthesis and physical properties of sulphonated poly(styrene ethylene/butylenes styrene), *Polymer*, 1991, 32, 10.

ASTM standard E 96-95. "Standard Test Methods for Vapor Transmission of Materials". American Society for Testing & Materials. Philadelphia, PA., 2002

"Handbook of Chemistry and Physics" 66th edition, CRC Press Inc. FL, 1985

"The Merk Index. An Encyclopedia of Chemicals, Drugs, and Biologicals", 13th edition, Merck & Co., Inc, Whitehouse Station, NJ, 2001.

Elabd, Y.A., Napadensky, E., Sloan, J.M., Crawford, D.M., Walker, C.W., in "Triblock copolymer ionomers membranes. Part I. Methanol and proton transport." *Journal of Membrane Science*, 217 (2003) 227-242.